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<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08G 63/60, C08L 67/04, C08J 5/18</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/26802</b> <b>(43) International Publication Date:</b> 24 November 1994 (24.11.94)
<b>(21) International Application Number:</b> PCT/US94/04964 <b>(22) International Filing Date:</b> 10 May 1994 (10.05.94)  <b>(30) Priority Data:</b> 08/061,064 14 May 1993 (14.05.93) US 08/187,674 27 January 1994 (27.01.94) US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventors:</b> SAMUELS, Michael, Robert; 5116 New Kent Road, Wilmington, DE 19808-2706 (US). WAGGONER, Marion, Glen; 36 Sageway Road, R.D. 3, Hockessin, DE 19707 (US).  <b>(74) Agents:</b> DUPLANTIER, Jon-Al et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LIQUID CRYSTALLINE POLYMER COMPOSITIONS  <b>(57) Abstract</b>  This invention relates to liquid crystalline polymers (LCPs) derived from (I) hydroquinone and/or 4,4'-biphenol and/or bis(4-hydroxyphenyl) ether, (II) terephthalic acid, (III) 2,6-naphthalene dicarboxylic acid and/or 4,4'-bibenzoic acid, (IV) 4-hydroxybenzoic acid, (V) 6-hydroxy-2-naphthoic acid, and optionally (VI) an aliphatic diol in specified ratios. In addition to forming exceptionally tough films, the LCPs are useful as molding resins or for blending with other thermoplastic polymers.		

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TITLE

## LIQUID CRYSTALLINE POLYMER COMPOSITIONS

BACKGROUND OF THE INVENTION

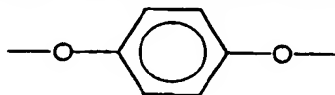
5 This invention relates to novel liquid crystalline polymer compositions, the melting points of which vary widely over the compositional range. This characteristic with respect to melting point makes the compositions particularly useful for blending with other polymers.

Liquid crystalline polymers ("LCPs"), including those made from a variety of aromatic diols, diacids and hydroxyacids, are known in the art. LCPs have varying physical properties, such as melting point (if any), heat deflection temperature, tensile strength, etc. Depending on these properties, LCPs are useful in many applications, such as molding resins, semipermeable membranes, blending, films, etc. The present invention relates to LCPs made from hydroquinone ("HQ") and/or 4,4'-biphenol ("BP") and/or bis(4-hydroxyphenyl) ether ("POP"), terephthalic acid ("TPA"), 2,6-naphthalene dicarboxylic acid ("NPA") and/or 4,4'-bibenzoic acid ("BB"), 4-hydroxybenzoic acid ("HBA"), 6-hydroxy-2-naphthoic acid ("HNA"), and optionally an aliphatic diol and another aromatic diacid in certain proportions. These LCPs are useful in typical LCP thermotropic applications, such as films and molding resins. In addition, these LCPs are useful for blending with other polymers, due to the melting point range mentioned above.

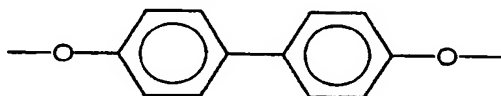
SUMMARY OF THE INVENTION

25 This invention relates to compositions comprising a liquid crystalline polymer comprising the following repeat units:

(I) at least one repeat unit selected from the group consisting of

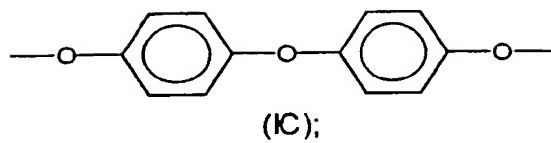


(IA),

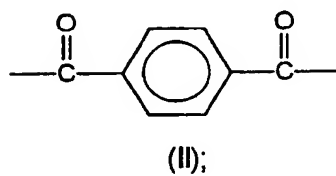


(IB), and

- 2 -

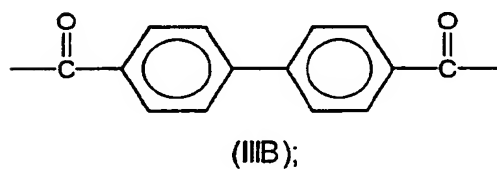
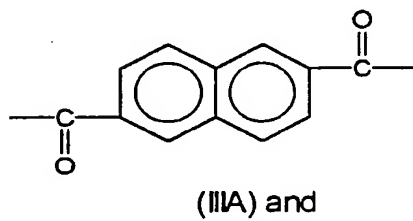


(II)



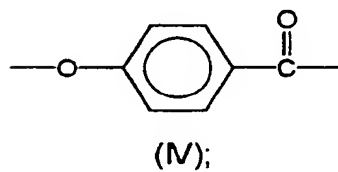
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(III) at least one repeat unit selected from the group consisting of



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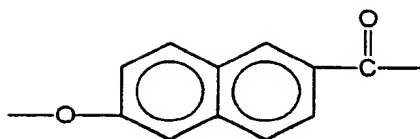
(IV)



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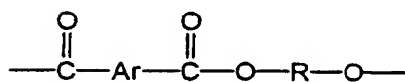
- 3 -

(V)



(V); and

5 (VI)



(VI)

wherein each Ar is independently a divalent aromatic radical, and each R is independently an alkylene radical containing 2 to 10 carbon atoms, and further wherein the molar ratio of (II) to (III) ranges from 25:75 to 90:10; the molar ratio of (I) to (II) + (III) is substantially 1:1; the molar ratio of (IV) to (V) ranges from 97:3 to 50:50; the number of moles of (IV) plus (V) ranges from 100 to 600 per 100 moles of (I); and provided that when

$$15 \quad \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} < 0.05,$$

the number of moles of (V) satisfies the following equation:

$$\text{number of moles of (V)} \leq \frac{8 + 0.04 [\text{number of moles of (IV)}]}{0.96},$$

and also provided that

$$20 \quad 0 \leq \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} \leq 0.40,$$

wherein (I), (II), (III), (IV), (V) and (VI) are in units of moles. Throughout this Application the number of moles of (I) is the total moles of (IA) plus (IB) plus (IC) and the total number of moles of (III) is the total moles of (IIIA) plus (IIIB).

### DETAILED DESCRIPTION

This invention relates to compositions comprising an LCP which is comprised of the repeat units given above. The molar ratio of repeat units (IA) to (IB) to (IC) ranges from 0:0:100 to 0:100:0 to 100:0:0. Preferably,

repeat units (IA) and (IB) are present, with the molar ratio of (IA) to (IB) ranging from 1:99 to 99:1. In the more preferred LCP, repeat units (IA) and (IB) are present, with the molar ratio of (IA) to (IB) ranging from 75:25 to 25:75.

5 In the preferred LCP, the molar ratio of (II):(III) ranges from 30:70 to 85:15. The preferred range of the molar ratio of (IV):(V) is from 50:50 to 90:10. The preferred range of the number of moles of (IV) plus (V), per 100 moles of (I), ranges from 200 to 500.

10 It is understood by the artisan that in order to readily form high molecular weight LCP, the molar ratio of the diols [i.e., (IA), (IB) and/or (IC)] to the diacids [i.e., (II) and (IIIA) and/or (IIIB)] present in the polymerization of monomers to form an LCP should be about 1:1. Small deviations from this ratio are not critical, but large deviations are normally to be avoided, since it usually prevents or slows polymerization to relatively  
15 high molecular weight.

The number of moles of (V) present in the instant LCPs satisfies the following equation A:

$$20 \quad \text{A. number of moles of (V)} > \frac{8 + 0.04 [\text{number of moles of (IV)}]}{0.96}$$

when

$$\frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} < 0.05,$$

wherein (I), (II), (III), (IV), (V) and (VI) are in units of moles.

25

In the preferred and most preferred LCPs, the number of moles of (V) satisfies the following equations B and C, respectively:

$$30 \quad \text{B. number of moles of (V)} > \frac{12 + 0.06 [\text{number of moles of (IV)}]}{0.94},$$

$$\text{C. number of moles of (V)} > \frac{16 + 0.08 [\text{number of moles of (IV)}]}{0.92}.$$

- 5 -

It is further preferred that when

$$\frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} < 0.10,$$

the amount of (V) is also controlled by equations A, B, or C.

5

In the above equations, the number of moles of (IV) and (V) is on the basis that the total number of moles of (I) + (II) + (III) is 200.

In other preferred LCPs,

10

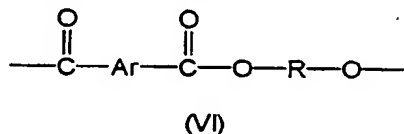
$$0 = \frac{(IC)}{(IA) + (IB) + (IC)}$$

and/or

$$0 = \frac{(IIIB)}{(IIIA) + (IIIB)}$$

15

The polymers of this invention may contain units (I)-(V). The polymers may also contain a repeat unit (VI) formally based on the formula



which can be thought of as the repeat unit of a partially aromatic polyester. By a "partially aromatic polyester" is meant a polyester based on one or  
20 more glycols containing 2 to 10 carbon atoms and an aromatic dicarboxylic acid (e.g., a diacid in which the carboxyl groups are bound directly to an aromatic ring). Such glycols include ethylene glycol, 1,4-butanediol, and 1,4-bis(hydroxymethyl)cyclohexane. Useful aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, 4,4'-bibenzoic acid, and 2,6-naphthalene  
25 dicarboxylic acid.

In preferred partially aromatic polyesters, Ar is 1,4-phenylene and R is ethylene [derived from poly(ethylene terephthalate)], or Ar is 1,4-phenylene and R is 1,4-butylene [derived from poly(butylene terephthalate)], or Ar is 2,6-naphthalene dicarboxylic acid and R is ethylene  
30 [derived from poly(ethylene 2,6-naphthalenedioate)] or Ar is 1,4-butylene [derived from poly(butylene terephthalate)]. It is to be understood that once these units are incorporated in the liquid crystalline polymer of the present

invention, the Ar and R portions of the unit may not necessarily be joined together, but may be randomly distributed through the liquid crystalline polymer.

5 The amount (in moles) of repeat unit (VI) in the polymer is governed by the equation

$$0 \leq \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} \leq 0.40,$$

10 The amounts of (I), (II), (III), (IV), (V) and (VI) are in units of moles. In a preferred liquid crystalline polymer, the amount of (VI) is governed by the equation

15 
$$0.050 \leq \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} \leq 0.20,$$

The repeat unit (VI) may be incorporated into the LCP by methods well known to the artisan. For instance, the partially aromatic polyester from which repeat unit (VI) is formally derived may be added to a polymerization in which the other repeat units are being polymerized from the monomers (or suitable derivatives thereof). Alternatively, (VI) may be incorporated into an already formed LCP by melt transesterification in a suitable mixer such as a twin screw extruder. The use of a transesterification catalyst is preferred. Sufficient transesterification is deemed to have taken place when the original melting points (assuming the partially aromatic polyester has a melting point) of the LCP and partially aromatic polyester cannot be detected by Differential Scanning Calorimetry (as measured by modified ASTM D3418-82, see below).

25 The LCPs of the present invention are useful as molding resins for molding electrical connectors, films, etc., and are especially useful for blending with other polymers. Generally speaking, when blending two polymers together, it is undesirable to greatly exceed the normal processing temperature of the polymer that would be processed at the lower temperature. For example, with a crystalline polymer, the normal processing temperature thereof would often be 10-30°C above its melting point. Such a limitation on processing temperature may be necessary, for



example, because the high temperature stability of the polymer may be limited. As shown in Figure 1, compositional variation in the instant LCPs, particularly variation in the amount of HBA and HNA, gives large changes in the melting point of the LCP. The melting point range of the present  
5 LCPs is generally at 200-300°C, which is a temperature range in which many commonly used polymers are processed. Blends of polymer with the instant LCPs are useful, for example, as molding resins and for films. The instant LCPs have good physical properties, such as tensile elongation, tensile strength, flexural strength, etc.

10 The instant LCPs may be made by methods readily available or well known to those skilled in the art. For example, acetate esters of the hydroxyl groups in the starting materials may be condensed with the carboxylic acids present in the monomers, which is the method used in the examples herein, or the phenyl esters of the carboxyl groups present in the  
15 monomers may be condensed with the hydroxyl groups in the monomers.

The LCPs described above can contain, or can be compounded with, other additives, ingredients, and modifiers known to be added to, or compounded into, LCPs, such as, but not limited to, fillers (such as glass), carbon fiber, catalysts, nucleants, pigments, antioxidants, stabilizers,  
20 plasticizers, lubricants, tougheners, minerals, carbon black, synergists, glass reinforcing agents, calcium metasilicate, calcium carbonate, talc, titanium dioxide, and calcined aluminum silicate.

Films made from the instant LCPs can be made using conventional methods including simple extrusion. Particularly good films  
25 are obtained by extrusion using the apparatus described in U.S. Patents 4,963,428 and 4,973,442 (especially Figures 3 and 6), the disclosures of which are hereby incorporated by reference. Preferred films are those exhibiting tensile elongations of at least twelve percent in the machine and/or transverse directions. In a more preferred embodiment, films exhibiting  
30 tensile elongations of at least twelve percent in the machine and/or transverse directions also exhibit a tensile modulus in the machine and/or transverse directions of at least 3.45 GPa (500,000 psi) and more preferably 5.51 GPa (800,000 psi).

35 The relative overall orientations of the LCP in the film can be varied by proper choice of the extrusion conditions (including die variables), and films with relatively balanced properties in the machine and transverse

direction can be obtained. Further, molecular orientation can be adjusted so that the predominant orientation is in the machine or transverse direction. By "balanced properties" is meant at least two of tensile strength, tensile modulus and tensile elongation of a particular film are within 20% (relative) of each other in the machine direction and transverse direction for each physical property.

### EXAMPLES

Abbreviations for the various monomers used in the Examples are as follows:

10	"HQ"	=	hydroquinone,
	"BP"	=	4,4'-biphenol,
	"TPA"	=	terephthalic acid,
	"NPA"	=	2,6-naphthalene dicarboxylic acid,
	"HBA"	=	4-hydroxybenzoic acid, (which contained 1,000-
15			1,600 ppm potassium), and
	"HNA"	=	6-hydroxy-2-naphthoic acid
	"BB"	=	4,4'-bibenzoic acid
	"POP"	=	bis(4-hydroxyphenyl) ether.

20           The amount, in relative moles, of each monomer used to make an LCP in the Examples is given in Table 2, below. Melting points ( $T_m$ ) were determined by ASTM D3418-82, at a heating rate of 25°C/min.  $T_m$  was measured on the as-made polymer (first heat). Heat deflection temperature (HDT) was measured by ASTM D648 at 1.8 MPa.

25           Acetic anhydride was present in all polymerizations in an amount of 3 to 10% molar excess based on hydroxyl groups present

### EXAMPLES 1-14

#### Preparation of the LCP

30           The LCPs in the Examples below were prepared as described below, wherein the values for X1 through X4 are provided in Table 1, below, and wherein the reactants, and amounts thereof, are provided in Table 2, below. The reactants were charged, in a nitrogen atmosphere, into a reaction vessel equipped with a Vigreux Column, condenser, and a stirrer (stir speed set at 125 RPM). The resultant reaction mixture was heated to  
35           reflux. Reflux began at a pot temperature of approximately 150°C. The reaction mixture was refluxed about forty minutes, at constant temperature.

During the next fifty minutes, the pot temperature was slowly raised to about X1, during which time acetic acid byproduct was removed. Pressure was then reduced over the next approximately X2 minutes to about 133 Pa (abs), while the stirrer speed was reduced to 20 RPM and the pot temperature increased to about X3. The polymerization was terminated approximately X4 hours after charging of the ingredients. The resultant product was removed from the reaction vessel with a scooping tool, rapidly cooled to room temperature, and ground.

#### Compounding of the LCP With Glass Fiber

The LCPs of Examples 1-4 were each compounded with glass fiber. Compounding was done in a 28 mm Werner and Pfleiderer twin screw extruder having a zone with conventional conveying elements, kneading, or mixing elements, along with a low pressure zone with venting under vacuum of any volatiles from the polymer melt and a die. As the compounded LCP compositions exited the die, they were quenched with a water spray and cut into pellets with a conventional strand cutter. The extruder barrel and die temperatures were maintained at about 290-320°C and 300-320°C, respectively.

#### Molding of LCP Compositions into Test Bars

Prior to molding, the LCP pellets were dried overnight for about 16 hours in a vacuum oven, with a nitrogen purge, at 100-130°C. The dried polymer pellets were molded into standard test bars, as required per ASTM D638 for determining tensile properties, on either a 42.5g Arburg molding machine or a 170g HPM molding machine, with barrel temperature settings of 330-360°C and injection pressures of 27-41 MPa. Examples 1-4 contained 30% glass fiber. Examples 5-14 were neat polymers.

#### Results

The LCPs were tested for melting point ( $T_m$ ) on the as made polymer and for HDT on molded polymer bars. The results are provided in Table 2, below.

Figures 1 and 2 show the results of statistical analyses of the melting points and HDT values obtained for Examples 6 to 14. The data were analyzed and plotted using a program from SYSTAT, Inc., Evanston, IL, U.S.A. called SYSTAT for Windows, Version 5, and using the contour plot routine. In Figure 1, the contour lines are constant melting point lines

(valued as indicated), while varying the HBA and HNA amounts in the LCPs. Figure 2 is similar, except the values used are HDTs (of neat LCP).

**Table 1**

5

Example	X1 Temp. after Reflux	X2 Vacuum Cycle	X3 Final Temp.	X4 Run Length
1	360	120	360	6
2	360	110	360	6.5
3	360	120	360	7
4	360	120	360	7
5	360	85	360	4.3
6	340	240	360	9
7	350	195	360	8.7
8	360	170	360	7.5
9	360	95	360	5.3
10	360	170	360	5.6
11	360	170	360	5.4
12	360	120	360	5
13	360	125	360	5
14	360	84	360	4.3

Table 2

Ex. No.	HQ	BP	TPA	NPA	HBA	HNA	Wt % Glass Fiber <sup>(1)</sup>	Tm	HDT
1	50	50	85	15	320	100	30	249	197
2	50	50	50	50	200	200	30	197	159
3	100	0	70	30	320	100	30	219	184
4	0	100	70	30	320	100	30	282	226
5	50	50	60	40	300	40	--	---	181
6	50	50	70	30	270	50	--	280	160
7	50	50	70	30	250	70	--	231	120
8	50	50	70	30	230	90	--	230	133
9	50	50	70	30	400	80	--	273	135
10	50	50	70	30	300	80	--	248	117
11	50	50	70	30	400	40	--	312	---
12	50	50	70	30	210	110	--	205	138
13	50	50	70	30	270	50	--	265	171
14	50	50	70	30	200	100	--	207	143

(1) based upon the weight of the LCP and glass fiber only.

5

EXAMPLES 15-19

Films were made from a polymer having the same composition as that of Example 6 above. The polymer had a melting point of about 266°C and contained no fillers.

10

Two different dies were used to make the films. For Example 15, a die similar to that shown in Figure 8 of U.S. Patent No. 4,973,442, and modified as described for thermotropic LCPs in U.S. Patent No. 4,963,428 ('428) at column 9, line 57 to column 10, line 55 was used. The die had the dimensions given in Table II of '428 as the "Xydar Die". Polymer was fed

15

into the die at a rate of 0.6 mL per revolution of the die by a 25 mm Berstorff co-rotating twin screw extruder. The heating zones of the extruder were set (from rear to front) at 260, 271, 279, 274 and 274°C. The die temperature was set at 279°C. Upon exiting the die, the polymer tube was

blown (with air) to a diameter of 20.3 cm. The resulting film tube was slit and tested in the machine and transverse directions. Additional data concerning the extrusion conditions are shown in **Table 3**, and film physical properties are shown in **Table 4**.

5 For Examples 16-19, films were made using a die similar to that shown in Figure 1 of WO 90/15706. Dimensions of Parts 32, 34 and 36 are as given in Table 2 of '428.

10 The polymer was fed into the die at a rate of 0.6 mL per revolution of the die by a 25 mm Berstorff co-rotating twin screw extruder. The heating zones of the extruder and die were the same as in Example 15. Upon exiting the die, the polymer tube was blown (with air) to a diameter of 7.6 cm. The resulting film tube was slit and tested in the machine and transverse directions. Additional data concerning the extrusion conditions are shown in **Table 3**, and film physical properties are shown in **Table 4**.

15 Tensile properties were determined by ASTM D882, using a testing speed of 10% of the initial gage length per minute. The initial gage length was 7.62 cm, and the width of the sample was 0.508 cm. Properties were measured in both the machine direction (MD) and the transverse direction (TD).

20

**Table 3**

Example No.	Die Rotation (rpm)	Takeup Speed m/min	Melt Temp. (°C)
15	8.5	2.9	299
16	8.0	5.3	311
17	8.0	10.4	311
18	4.0	2.5	311
19	1.5	1.0	311

**Table 4**

Example No.	Film Thickness (mm)	Test Direction	Modulus (GPa)	Tensile Strength (MPa)	Percent Elongation at Break
15	0.051	MD	8.20	224	12.5
		TD	7.17	217	12.8
16	0.025	MD	17.2	315	6.1
		TD	6.48	162	8.0
17	0.018	MD	40.7	430	1.4
		TD	2.27	48.9	9.7
18	0.051	MD	8.68	205	15.0
		TD	6.61	176	13.3
19	0.18	MD	3.58	91.6	19.1
		TD	10.4	247	7.9

5

**EXAMPLE 20**

The polymer used in Example 20 had HQ/BP/TPA/NPA/HBA/HNA molar ratios of 50/50/70/30/270/50, and had a melting point of about 276°C. A sample of this polymer was extruded through a 28 mm Werner & Pfleiderer twin screw extruder equipped with an adjustable slit die that was 25.4 cm wide and the slit of which was adjusted to give a film about 0.9 mm thick. All of the barrel heating zones were set to 270°C, except for the rear zone which was set to 220°C. The film was drawn slightly on exiting the die. The resulting film was relatively tough in both the machine and transverse directions.

15

**EXAMPLES 21-23**

For each of the LCP compositions in Examples 21-23, the reactants, including the partially aromatic polyester, were charged into a reaction vessel equipped with a Vigreux column, condenser, and a stirrer (speed set at 50 rpm). The reactants initially charged are listed in **Table 5**. The resultant reaction mixture was heated to reflux. Reflux began at a pot temperature of between 155°C and 160°C. The reaction mixture was refluxed for about 40 minutes, at a constant pot temperature of about 170°C.

20

After the total reflux was completed, the pot temperature was raised to 190°C, and removal of by-product acetic acid began. Thereafter, while continuing to remove acetic acid, the temperature was increased by 20°C increments at 20 minute intervals, until the temperature had reached 305°C.

- 5 A vacuum was then applied to reduce the pressure to about 80 kPa (absolute). The pressure was further reduced in 16.7 kPa increments every 10 minutes until a pressure of 16.7 kPa was reached. Thereafter, in the next three 10 minute intervals, the pressure was reduced to 6.7 kPa, 2.7 kPa and finally, to full vacuum (less than 13.3 Pa absolute). As the viscosity
- 10 increased, the stirrer speed was reduced to about 30 rpm. The polymerization was terminated when the melt viscosity was greater than or equal to 25 Pa·s at 365°C and 1000 sec<sup>-1</sup> shear rate. The total reaction time after the components were initially charged into the reaction vessel was approximately 7-8 hours. The melting points of the resulting polymers are
- 15 shown in Table 5.

Table 5

Example No.	HQ (g)	BP (g)	TPA (g)	NPA (g)	HBA (g)	HNA (g)	Partially Ar. Polyester (g)	Tm (°C)
21	63.1	106.8	133.4	74.4	427.8	107.9	44.0 (PET)	265
22	60.0	101.5	126.8	70.7	406.7	102.6	83.8 (PET)	247
23	58.5	99.0	123.6	69.0	396.5	100.0	102.9 (PEN)	194, 222

- 20 PET = poly (ethylene terephthalate)  
 PEN = poly (ethylene 2,6-naphthalenedioate)



**EXAMPLES 24-26**

The polymers of Examples 24-26 were made by the same method used for Examples 21-23. Monomers used for the polymerizations are shown in **Table 6**, along with the melting point of the polymers.

5

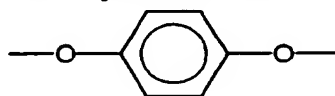
**Table 6**

Ex. No.	HQ (g)	BP (g)	TPA (g)	NPA (g)	HBA (g)	HNA (g)	Other (g)	Tm (°C)
24	63.5	107.4	103.8	0	477.9	86.8	122.7 (BB)	268.8
25	115.0	0	117.7	33.9	461.7	196.6	41.7 (BB)	275.2
26	52.5	88.7	138.5	77.3	444.3	112.1	48.2 (POP)	245.0

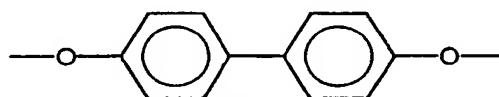
**WHAT IS CLAIMED IS:**

1. A composition comprising a liquid crystalline polyester (LCP) that comprises the following repeat units:

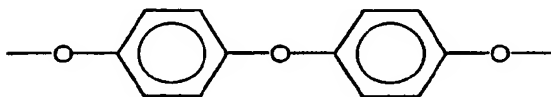
5 (I) at least one repeat unit selected from the group consisting of



(IA),



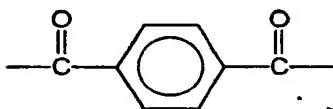
(IB), and



(IC);

10

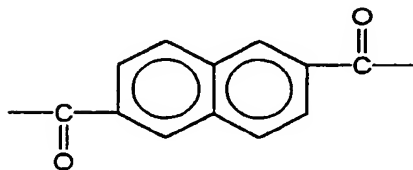
(II)



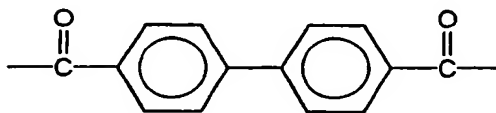
(II);

(III) at least one repeat unit selected from the group consisting of

15



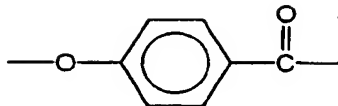
(IIIA) and



(IIIB);

- 17 -

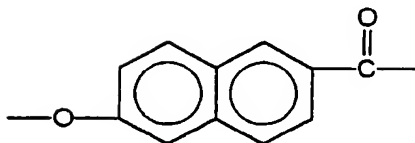
(IV)



(M);

5

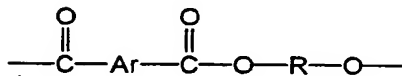
(V)



(V); and

10

(VI)



(VI)

wherein each Ar is independently a divalent aromatic radical, and each R is  
 15 independently an alkyne radical containing 2 to 10 carbon atoms, and  
 further wherein the molar ratio of (II) to (III) ranges from 25:75 to 90:10;  
 the molar ratio of (I) to (II) + (III) is substantially 1:1; the molar ratio of (IV)  
 to (V) ranges from 97:3 to 50:50; the number of moles of (IV) plus (V)  
 ranges from 100 to 600 per 100 moles of (I); and provided that when

20

$$\frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} < 0.05,$$

the number of moles of (V) satisfies the following equation:

$$\text{number of moles of (V)} > \frac{8 + 0.04 [\text{number of moles of (IV)}]}{0.96},$$

and also provided that

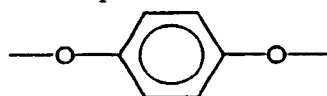
$$0 \leq \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} \leq 0.40,$$

wherein (I), (II), (III), (IV), (V) and (VI) are in units of moles.

5

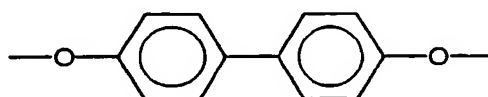
2. A composition comprising a liquid crystalline polyester (LCP) that consists essentially of the following repeat units:

(I) at least one repeat unit selected from the group consisting of

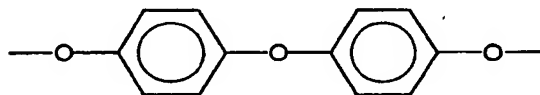


(IA),

10



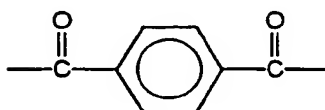
(IB), and



(IC);

15

(II)

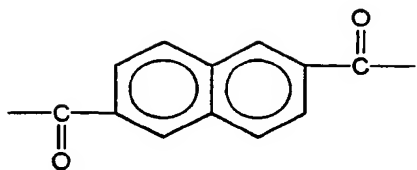


(II);

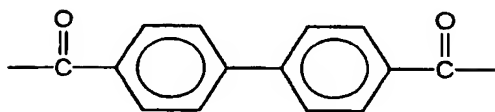
(III) at least one repeat unit selected from the group consisting of

20

- 19 -



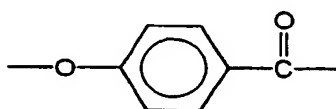
(III A) and



(III B);

5

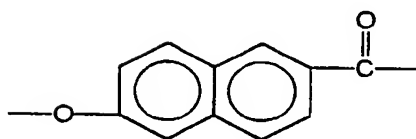
(IV)



(IV);

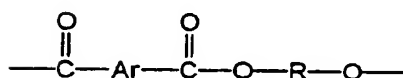
(V)

10



(V); and

(VI)



(VI)

15

wherein each Ar is independently a divalent aromatic radical, and each R is independently an alkylene radical containing 2 to 10 carbon atoms, and

further wherein the molar ratio of (II) to (III) ranges from 25:75 to 90:10; the molar ratio of (I) to (II)+(III) is substantially 1:1; the molar ratio of (IV) to (V) ranges from 97:3 to 50:50; the number of moles of (IV) plus (V) ranges from 100 to 600 per 100 moles of (I); and provided that when

$$5 \quad \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} < 0.05,$$

the number of moles of (V) satisfies the following equation:

$$\text{number of moles of (V)} > \frac{8 + 0.04 [\text{number of moles of (IV)}]}{0.96},$$

10 and also provided that

$$0 \leq \frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} \leq 0.40,$$

wherein (I), (II), (III), (IV), (V) and (VI) are in units of moles.

15 3. The composition of Claim 2 wherein

$$\frac{(VI)}{(I) + (II) + (III) + (IV) + (V) + (VI)} = 0,$$

$$20 \quad \frac{(IC)}{(IA) + (IB) + (IC)} = 0 \quad \text{and}$$

$$\frac{(IIIB)}{(IIIA) + (IIIB)} = 0$$

25

4. The composition of Claim 3 wherein (IA) and (IB) are both present and the molar ratio of (IA) to (IB) ranges from 99:1 to 1:99.

30 5. The composition of Claim 4 wherein the molar ratio of (IA) to (IB) ranges from 75:25 to 25:75.

6. The composition of Claim 3 wherein the molar ratio of (II) to (III) ranges from 30:70 to 85:15.

35 7. The composition of Claim 3 wherein the molar ratio of (IV) to (V) ranges from 50:50 to 90:10.

8. The composition of Claim 3 wherein the number of moles of (IV) plus (V) is 200 to 500 per 100 moles of (I).

5 9. The composition of Claim 8 wherein (IA) and (IB) are both present and the molar ratio of (IA) to (IB) ranges from 75:25 to 25:75, the molar ratio of (II) to (III) ranges from 30:70 to 85:15, and the molar ratio of (IV) to (V) ranges from 50:50 to 90:10.

10 10. The composition of Claim 2 wherein the amount of (V) satisfies the following equation:

$$\text{number of moles of (V)} > \frac{12 + 0.06 [\text{number of moles of (IV)}]}{0.94}$$

15 11. The composition of Claim 3 wherein the amount of (V) satisfies the following equation:

$$\text{number of moles of (V)} > \frac{12 + 0.06 [\text{number of moles of (IV)}]}{0.94}$$

20 12. The composition of Claim 2 further comprised of at least one of fillers, carbon fiber, catalysts, nucleants, pigments, antioxidants, stabilizers, plasticisers, lubricants, tougheners, minerals, carbon black, synergists, glass reinforcing agents, calcium metasilicate, calcium carbonate, talc, titanium dioxide, and calcined aluminum silicate.

25 13. The composition of Claim 2 wherein the amount of (VI) present satisfies the following equation:

$$0.050 \leq \frac{(\text{VI})}{(\text{I}) + (\text{II}) + (\text{III}) + (\text{IV}) + (\text{V}) + (\text{VI})} \leq 0.20.$$

30 14. The composition of Claim 2 wherein Ar is selected from 1,4-phenylene or 2,6-naphthalene and R is selected from ethylene or 1,4-butylene.

35 15. The composition of Claim 13 wherein Ar is selected from 1,4-phenylene or 2,6-naphthalene and R is selected from ethylene or 1,4-butylene.

16. A film comprising the composition of Claim 1.

17. A film comprising the composition of Claim 2.

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18. A film comprising the composition of Claim 3.

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Figure 1  
MELTING POINT  
(50/50-70/30//HBA//HNA)

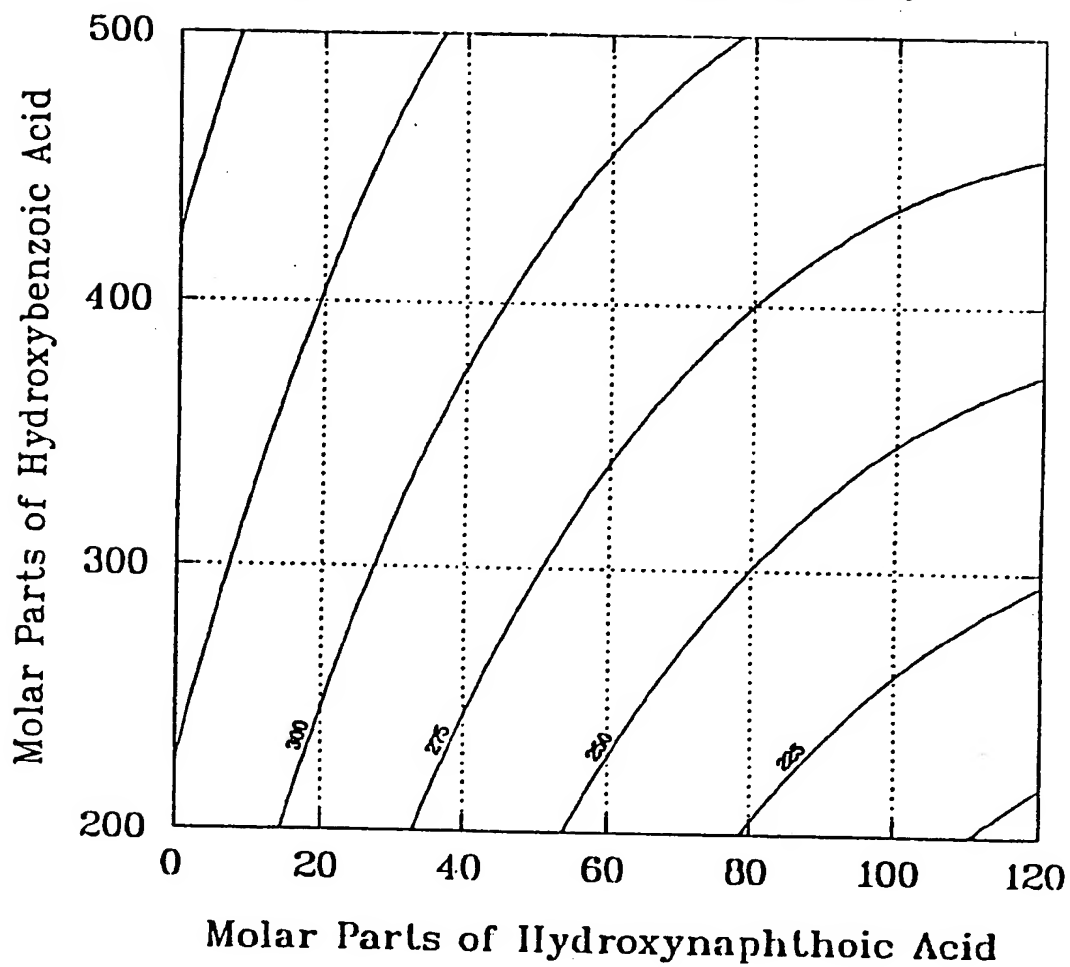
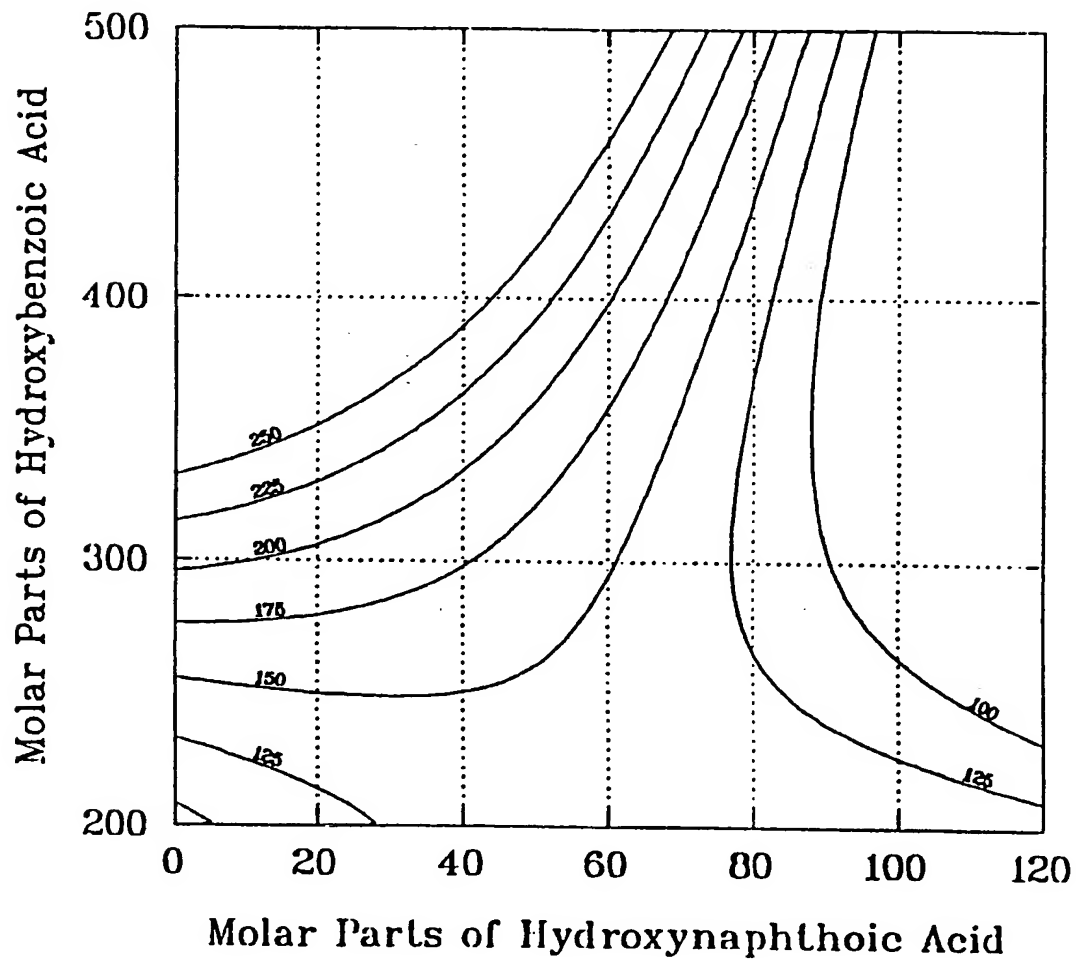


Figure 2  
HEAT DEFLECTION TEMPERATURES  
(50/50-70/30//HBA//HNA)



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/04964

## A. CLASSIFICATION OF SUBJECT MATTER

C 08 G 63/60, C 08 L 67/04, C 08 J 5/18

According to International Patent Classification (IPC) or to both national classification and IPC <sup>5</sup>

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 G 63/00, C 08 L 67/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4 983 713 (HAYASHI et al.) 08 January 1991 (08.01.91), examples 3,7; claim 1; column 6, lines 32-39. --	1-3, 8,16- 18
A	US, A, 4 473 682 (CALUNDANN et al.) 25 September 1984 (25.09.84), claim 1; examples; abstract. --	1,2, 16,17
A	US, A, 5 171 823 (CHARBONNEAU et al.) 15 December 1992 (15.12.92), claim 1; examples; column 7, lines 5-8. --	1,2, 16,17
A	US, A, 5 025 082 (KISHIRO et al.) 18 June 1991	1,2, 16,17

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

19 August 1994

Date of mailing of the international search report

09.09.94

Name and mailing address of the ISA

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Fax (+31-70) 340-3016

Authorized officer

KALTENEGGER e.h.

# INTERNATIONAL SEARCH REPORT

-2-

Inter nal Application No  
PCT/US 94/04964

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>(18.06.91), claim 1; examples 1,5-10,24; comparative example 4 (table 4); abstract. -----</p>	

## ANHANG

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

## ANNEX

to the International Search  
Report to the International Patent  
Application No.

## ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 94/04964 SAE 90188

In diesem Anhang sind die Mitglieder  
der Patentfamilien der im obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
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La présente annexe indique les  
membres de la famille de brevets  
relatifs aux documents de brevets cités  
dans le rapport de recherche inter-  
national visée ci-dessus. Les renseigne-  
ments fournis sont donnés à titre indica-  
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In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4983713	08-01-91	EP A2 350222 EP A3 350222 JP A2 2016120	10-01-90 27-02-91 19-01-90
US A 4473682	25-09-84	DE C0 3368422 EP A1 102160 EP B1 102160 JP A2 59062630 JP B4 4071091 US A 4522974	29-01-87 07-03-84 17-12-86 10-04-84 12-11-92 11-06-85
US A 3171923	15-12-92	keine - none - rien	
US A 5025082	18-06-91	EP A2 356226 EP A3 356226 JP A2 2294329 JP A2 2102223 JP A2 2058537	28-02-90 29-07-92 05-12-90 13-04-90 27-02-90

